



Preparation of copper-containing mesoporous manganese oxides and their catalytic performance for CO oxidation

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ARTICLE INFO

Article history:

Received 18 April 2008

Received in revised form 19 November 2008

Accepted 23 December 2008

Available online 31 December 2008

Keywords:

Manganese oxide

Mesoporous

CO oxidation

Lattice oxygen

Copper

ABSTRACT

Copper-containing mesoporous manganese oxides were prepared by the sol–gel method. The samples obtained were characterized by XRD, N₂ adsorption–desorption, ICP, CO-TPD, redox measurement and XPS. After calcination at 300 °C, amorphous structure was shown by XRD for all the samples. All the samples had mesopores of about 6 nm and high surface areas of 170–230 m² g^{−1}. Using these samples as catalysts, CO oxidation was carried out as a model reaction. Copper-containing mesoporous manganese oxide prepared by the sol–gel method showed a very high activity. On the other hand, copper-supported manganese oxide prepared by the impregnation method using copper sulfate showed a low activity. Differences in activities were correlated with the mobility of lattice oxygen.

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1. Introduction

Porous materials are industrially important and are used for separation, adsorption, catalysts and supports. These materials are characterized by their pore-structure such as pore diameter and pore-size distribution. Mesoporous materials have generally a large surface area and mesopores ranging from 2 to 50 nm in diameter. A new family of mesoporous material designated as M41S has been developed [1,2]. Since then, mesoporous silica and other mesoporous materials have received much attention [3–6]. On the other hand, the transition metal oxides play an important role as they are applied to catalysts, sensors and so on based on their chemical and/or physical properties [7–9]. Attempts to introduce the transition metal into the mesoporous silica frame have been performed, and a lot of researches have been reported [10–14]. Further, the mesoporous materials composed only of the transition metal oxides became synthesized [15–19].

On the other hand, the oxidation of carbon monoxide (CO) at low temperatures is a recent topic, because it is important for a cleaner exhaust gas, e.g. in automobile or industrial emission control, and also for pure hydrogen for the fuel cell [20–23]. The well-known example of the catalyst for CO oxidation is Hopcalite, which is based on manganese–copper mixed oxide. Hopcalite has cost-competitiveness and has been widely used for the respiratory system [24–27].

In this paper, we studied preparation and characterization of mesoporous manganese oxide and copper-containing mesoporous manganese oxide. CO oxidation was chosen as a model reaction to evaluate prepared manganese compounds as an oxidation catalyst.

2. Experimental

2.1. Preparation of catalysts

Into 50 mL of distilled water, 10 mmol of potassium permanganate was dissolved and 1.25–10 mmol of CuSO₄·5H₂O in 50 mL of distilled water was added into the former solution. Then, 3.3 mmol of maleic acid in 50 mL of distilled water was added as a reducing agent and the mixture was stirred for 1 h. After aging for 24 h at room temperature, thus produced black or brown gel was washed with distilled water. After drying at 70 °C overnight, copper-containing mesoporous manganese oxide (Cu/Mn (molar ratio) = 1/1–1/8) was obtained by calcination in air at 300 °C for 2 h.

In addition, mesoporous manganese oxide without copper was also prepared (Meso-Mn) [28]. By impregnating mesoporous manganese oxide with aqueous CuSO₄·5H₂O solution, copper-supported mesoporous manganese oxide (Cu loading: 2 or 7 wt%) was also prepared for reference. The catalysts prepared were reserved in capped glass sample holders placed in a desiccator.

Further, a commercial copper-containing manganese oxide, Hopcalite (Hopcalite 8–14 #) kindly provided by GL Sciences Inc. (Japan), was also used as a reference catalyst.

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2.2. CO oxidation

CO oxidation was performed in a fixed-bed flow-type reactor with 0.020 g of the prepared catalyst. After *in situ* pre-treatment at 300 °C for 30 min under N₂ stream, the temperature was decreased to room temperature. Then, the reaction was started at the total flow rate of 50 mL min⁻¹ (1 vol% CO, 20 vol% O₂ and balance N₂) controlled by three mass flow meters. The effluent gas was analyzed by GC (SHIMADZU, GC-14B equipped with Porapak Q and Molecular Sieves). Then, amounts of CO, CO₂ and O₂ were measured by the absolute calibration method.

2.3. Characterization of catalysts

The powder X-ray diffraction (XRD) patterns were obtained with JEOL JDX-3530 with Cu K α radiation at 40 kV and 20 mA. N₂ adsorption–desorption isotherms were obtained with BEL JAPAN BELSORP-mini2 and the pore size distribution (BJH method) and BET surface area were calculated based on the adsorption–desorption isotherms. The elemental analysis was carried out by SHIMADZU ICPS-1000III. Thermal desorption of CO was studied by the temperature-programmed desorption (TPD) method on BEL JAPAN TPD-1AT. For CO-TPD, the sample was pre-treated at 300 °C for 2 h in He, and then CO was contacted with the sample at room temperature for 1 h. After purging extra CO for 30 min, TPD measurement from room temperature to 800 °C was conducted. The gases evolved, namely CO, CO₂ and H₂O, were measured by the quadrupole mass spectrometer. Redox behavior was analyzed on SHIMADZU DTG-60H. For redox characterization, the sample of ca. 10 mg was pre-treated *in situ* at 300 °C for 2 h in 100 mL min⁻¹ of Ar, and the temperature was decreased to 200 °C in the same Ar flow. Then the reduction was carried out in 10 mL min⁻¹ of CO and 90 mL min⁻¹ of Ar for 30 min. After purging CO with Ar, the oxidation at the same temperature was carried out in 50 mL min⁻¹ of air (10 mL min⁻¹ of O₂) and 50 mL min⁻¹ of Ar for 30 min. This reduction–oxidation was repeated three times. X-ray photoelectron spectra (XPS) were recorded by JEOL JPS-9000MX with Mg K α radiation at 10 kV and 10 mA using C_{1s} 284.2 eV as an internal standard.

3. Results and discussion

3.1. Catalytic activity

The result of CO oxidation reaction (Fig. 1) reveals that copper-containing mesoporous manganese oxide prepared by the sol–gel

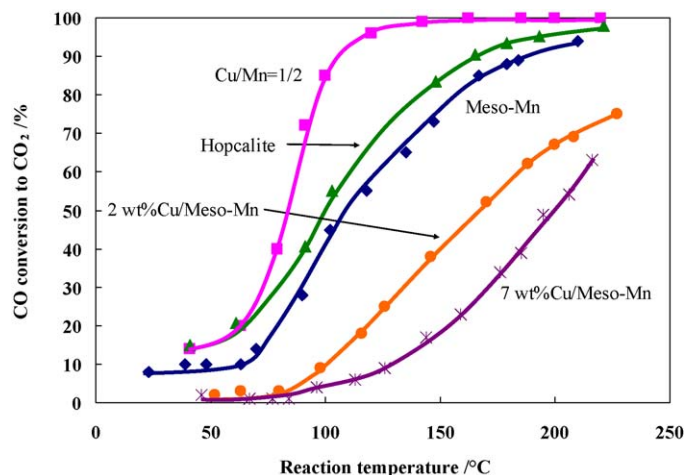


Fig. 1. CO oxidation reaction with various manganese oxides. Catalyst: 0.020 g, total flow rate: 50 mL min⁻¹ (1% CO, 20% O₂ and balance N₂).

method (Cu/Mn = 1/2) showed a higher activity than Hopcalite, which is the commercial CO oxidation catalyst. On the other hand, copper-supported mesoporous manganese oxides showed a lower activity than the support itself, namely mesoporous manganese oxide (Meso-Mn). Therefore, the cause of high activity of the samples prepared by the sol–gel method was supposed to be the synergy between copper and manganese based on high dispersion of copper in manganese oxide matrix. On the other hand, the reason for low activity of the copper-supported mesoporous manganese oxide was considered to be the surface area decrease by copper on the surface of Meso-Mn (*vide infra*). This further means that copper itself has no or little activity for CO oxidation under the conditions adopted. On the other hand, it was supposed that SO₄²⁻ contained in the copper source might have remained in the catalyst and influenced the catalytic activity. Therefore, the copper-containing mesoporous manganese oxide was prepared by the same method using Cu(NO₃)₂·3H₂O instead of CuSO₄·5H₂O and tested for CO oxidation. The result for CO oxidation was the same as that of the catalyst prepared using CuSO₄·5H₂O. This indicates that even if SO₄²⁻ might remain in the catalyst, it did not act as a poison or a promoter.

By the way, the raw material used for impregnation of copper was CuSO₄·5H₂O and it was supposed that the use of this salt was inadequate because of its high thermal stability. Then, Cu(NO₃)₂·3H₂O was used to prepare copper-supported mesoporous manganese oxide. Thus prepared 7 wt% Cu/Meso-Mn showed moderate activity between copper-containing mesoporous manganese oxide (Cu/Mn = 1/2) and Meso-Mn. So, an additional study on copper-supported mesoporous manganese oxide is under way.

It is reported that Hopcalite is weak to moisture [26]. To evaluate the influence of moisture, the performance of typically dried copper-containing mesoporous manganese oxide (Cu/Mn = 1/2) and the wet counterpart was compared (Table 1). The wet catalyst (sample B) kept for about two months in a capped glass sample holder under ambient atmosphere contained a large amount, about 15 wt%, of water. As indicated, the activity of sample B was lower than the fresh catalyst (sample A). Sample C is the catalyst treated at 300 °C for 30 min in air after CO oxidation using sample B. Although the activity of sample C was still a little lower than that of sample A, recovery of the catalytic activity is clearly observed. From these results, it would be expected if proper precaution is adopted against moisture, the copper-containing mesoporous manganese oxide could be used for the reaction.

Fig. 2 shows the influence of Cu/Mn molar ratio on the temperature for 50% CO conversion for the samples prepared by the sol–gel method. The Cu/Mn molar ratio is based on the elemental analysis and Fig. 2 reveals that the ratio observed was smaller for the real catalyst than that for preparation, especially for the catalysts of higher Cu/Mn ratios. By incorporation of copper up to the ratio of Cu/Mn = 1/3, CO oxidation activity was enhanced prominently. With higher copper incorporation than Cu/Mn = 1/3, the activity remained the same. To understand the activity difference among catalysts, properties of catalysts were studied.

Table 1

Influence of water on the temperature for 50% CO conversion for copper-containing mesoporous manganese oxide (Cu/Mn = 1/2).

	Temperature for 50% CO conversion (°C)
Sample A	83
Sample B	94
Sample C	89

Catalyst: 0.020 g (dry basis). Total flow rate: 50 mL min⁻¹ (1% CO, 20% O₂ and balance N₂). Sample A: fresh catalyst (*in-situ* pre-treatment at 300 °C for 30 min in N₂). Sample B: wet sample A with 15 wt % water (no *in-situ* pre-treatment). Sample C: catalyst treated at 300 °C for 30 min in air after CO oxidation using sample B.

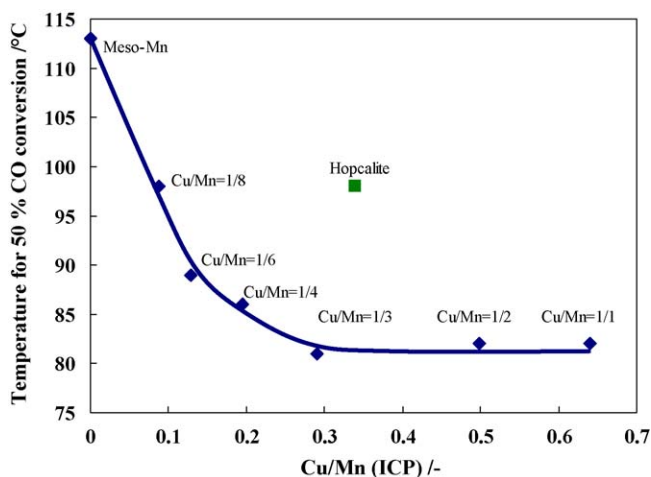


Fig. 2. Influence of Cu/Mn molar ratio on the temperature for 50% CO conversion for the samples prepared by the sol-gel method. Conditions are the same as in Fig. 1.

3.2. Characterizations and their relation to activity

All the XRD patterns of the samples prepared by the sol-gel method and the impregnation method gave no distinct peaks (Fig. 3). This means that catalysts are amorphous and copper is well mixed or dispersed with manganese even for catalysts prepared by impregnation. Hopcalite was also amorphous. Reddy et al. [29] studied similar copper manganese mixed oxide and their XRD patterns indicated crystalline hausmannite structure. This may be because of their preparation method, namely co-precipitation, or their high temperature calcination. The surface area of the sample prepared by the sol-gel method was about $200 \text{ m}^2 \text{ g}^{-1}$. By increasing Cu/Mn ratio, a minor decrease of the surface area was observed to about $180 \text{ m}^2 \text{ g}^{-1}$. Impregnation of copper to 7% vastly reduced the surface area by about 40%.

Figs. 4 and 5 show the N_2 adsorption-desorption isotherms and the pore size distributions, respectively. The adsorption-desorption isotherms of IUPAC Type IV hysteresis were obtained. In the case of the sol-gel method, by incorporation of copper, the pore size distributions were widened and the pore volumes decreased. On the other hand, in the case of catalysts prepared by the impregnation method, the type of adsorption-desorption isotherm and peak top position of the pore size distribution were similar to those of the parent mesoporous manganese oxide, simply decreasing the pore volume. All the mesoporous manganese oxides had pores of about 5–6 nm in diameter.

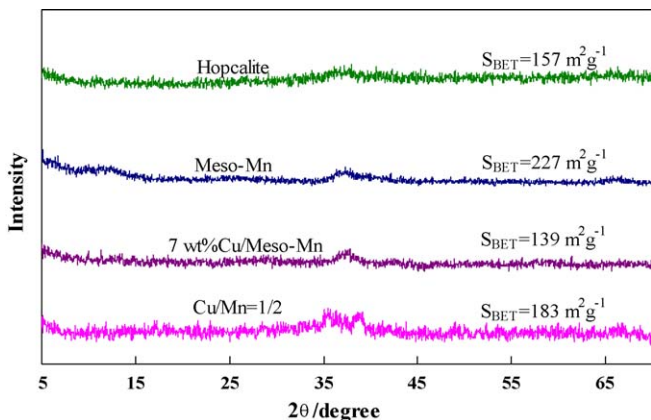


Fig. 3. XRD patterns and surface areas of various manganese oxides.

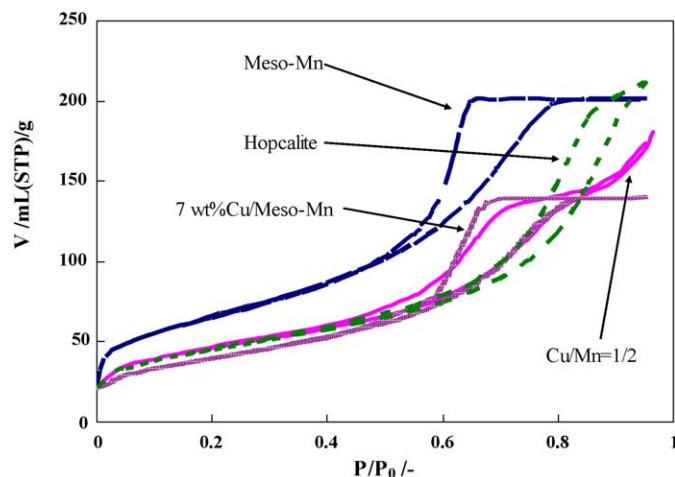


Fig. 4. N_2 adsorption-desorption isotherms of various manganese oxides.

Here, we would like to consider the relationship between CO oxidation activity and physical properties measured. Firstly, the lower activity for catalysts prepared by impregnation could be explained by the decrease of the surface area. Hopcalite did not have substantial mesopores, compared to other catalysts. However, Hopcalite showed better activity than Meso-Mn. Therefore, the surface area and the pore size distribution are not always the crucial factor to decide the catalytic activity, and other reasons should be explored.

Then, we considered that the cause of high activity for CO oxidation reaction was the synergy between copper and manganese, which influenced mobility of lattice oxygen. So, we studied the temperature-programmed desorption of CO (CO-TPD) and redox properties of catalysts using CO as a reducing gas and O_2 as an oxidizing gas. Fig. 6 shows the result of CO-TPD. As a desorbing gas, CO_2 was mainly detected with a minor amount of CO. As the measurement was conducted in the stream of He, desorption of CO_2 indicates oxidation of CO by the lattice oxygen. Copper-containing mesoporous manganese oxide prepared by the sol-gel method (Cu/Mn = 1/2) showed the highest CO_2 desorption. At least, three desorption peaks were observed at about 100, 200, and 500°C , suggesting three kinds of lattice oxygen of different environment. Hopcalite having Cu/Mn ratio of 1/3 did not show the 500°C desorption peak. In case of Meso-Mn, a small amount of CO_2 desorption was observed at around 100°C . These results suggest that the incorporation of copper accelerated the mobility of lattice

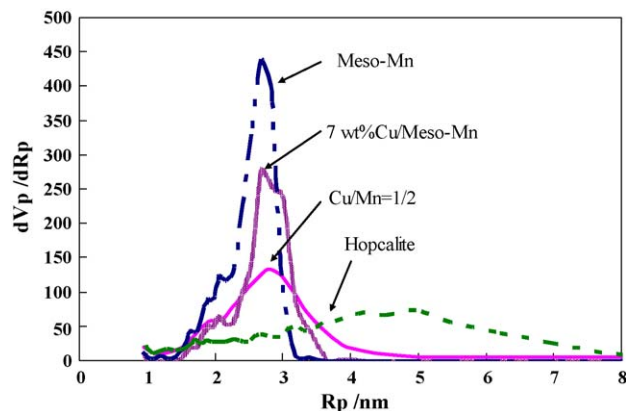


Fig. 5. Pore size distribution of various manganese oxides.

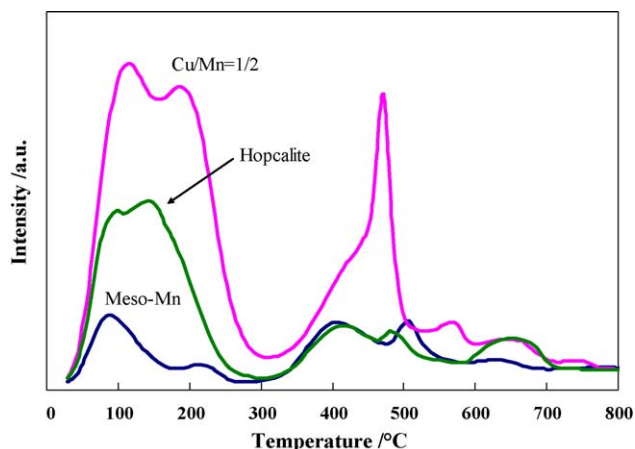


Fig. 6. CO-TPD of various manganese oxides ($m/z = 44$). Catalyst: 0.050 g (pre-oxygen). What should be stressed is that a large amount of the lattice oxygen of Cu/Mn = 1/2 were removed easily even at around room temperature.

Table 2 shows the result of redox measurement. Firstly, the catalyst was reduced and then oxidized, and this operation was repeated three times. The results of the redox measurement concerning the mobility of lattice oxygen were similar to those of CO-TPD. Namely, both the weight loss and increase of the copper-containing mesoporous oxide (Cu/Mn = 1/2) were almost double of those for Hopcalite, and far larger than those for Meso-Mn without copper. In addition, not only the amount of weight loss or increase, but also the rate of reoxidation was faster for copper-containing mesoporous manganese oxide prepared by the sol-gel method (Cu/Mn = 1/2). Consequently, in case of copper-containing mesoporous manganese oxides, redox of the catalysts proceeded smoothly. In other words, the lattice oxygen is highly mobile and this caused the higher CO oxidation activity.

XPS spectra of Mn $2p_{3/2}$ orbital are shown in Fig. 7. The binding energy of $2p_{3/2}$ peak for the manganese cations in MnO, Mn_3O_4 , Mn_2O_3 and MnO_2 are 640.9, 641.7, 641.8 and 642.4 eV, respectively [29]. Mn $2p_{3/2}$ peaks of mesoporous manganese oxide and copper-containing mesoporous manganese oxide were 642.1 and 641.5 eV, respectively. By incorporating copper, the binding energy of Mn shifted to the lower energy side. The binding energy of Mn of Hopcalite, the reference catalyst, was 641.8 eV. In order to determine the oxygen content and average valence of manganese of Meso-Mn, iodometric titration was performed, as previously described in the literature [30]. The average valence of manganese of Meso-Mn was measured to be 3.8. Therefore, the binding energy of Mn $2p_{3/2}$ at 642.1 eV of Meso-Mn seems to indicate the presence of Mn^{4+} and that at 641.5 or 641.8 eV of copper-containing mesoporous manganese oxide may suggest the presence of lower valence manganese ion(s). Fig. 8 showed XPS spectra of Cu $2p_{3/2}$ orbital. The binding energies of Cu $2p_{3/2}$ of copper cations in CuO and Cu_2O are about 933.2 and 932.3 eV, respectively [31]. Both of the Cu $2p_{3/2}$ peaks of copper-containing mesoporous manganese

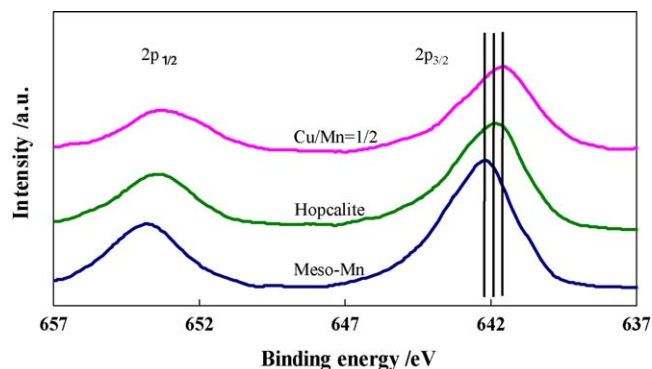


Fig. 7. Mn 2p XPS spectra of various manganese oxides.

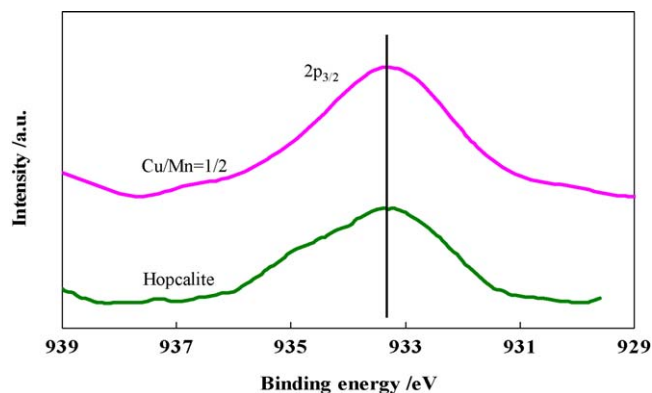


Fig. 8. Cu 2p XPS spectra of copper-containing mesoporous manganese oxides.

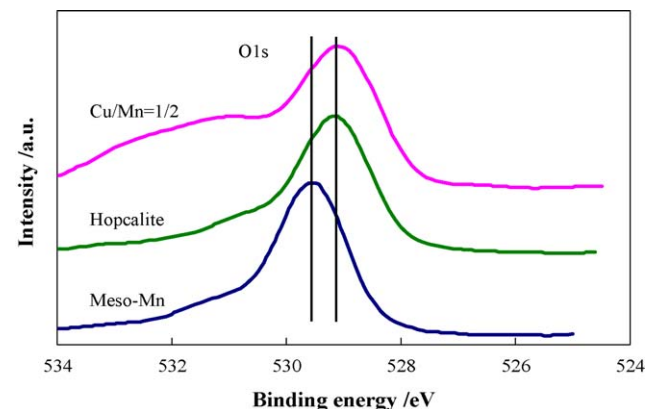


Fig. 9. O 1s XPS spectra of various manganese oxides.

and of Hopcalite were at 933.2 eV, meaning that electron density on copper cation is the same. Fig. 9 shows XPS spectra of O 1s orbital. The binding energies of O 1s of mesoporous manganese oxide and copper-containing mesoporous manganese oxide were 529.6 and 529.1 eV, respectively. By incorporating copper, the

Table 2
Redox property of various manganese oxides.

	First		Second		Third	
	Reduction weight loss (%)	Oxidation weight increase (%)	Reduction weight loss (%)	Oxidation weight increase (%)	Reduction weight loss (%)	Oxidation weight increase (%)
Cu/Mn = 1/2	13.9	9.6	10.7	9.9	10.0	8.8
Hopcalite	5.8	4.0	4.5	4.2	4.8	4.4
Meso-Mn	4.6	2.6	3.0	2.5	1.9	1.5

Reduction: 10% CO in Ar, total flow rate 100 mL min⁻¹. Oxidation: 10% O₂ in Ar, total flow rate 100 mL min⁻¹. Temperature: 200 °C.

binding energy of O 1s shifted to the low energy side. However, the point that should be paid more attention to is the high energy side. A broad peak ranging from about 530 to 534 eV could be observed. This peak was largest for the copper-containing mesoporous manganese oxide (Cu/Mn = 1/2) and also in Hopcalite the same but of moderate size could be observed. As stated above, the 2p_{3/2} peak of Mn and O 1s peak at 529 eV shifted to the lower energy side compared to those of Meso-Mn. This means that the electron density on these elements decreased. Therefore, there should exist an element that donated electron density and the only element judged from XPS measurement that donated the electron density is the oxygen ion. At present, the role of copper is not clear for the transfer of the electron density, because this binding energy shift was caused by incorporation of copper. However, it may be suggested that at least two kinds of oxygen species existed in the copper-containing mesoporous manganese oxide and one of these oxygen species, probably the higher binding energy species, was responsible for the more mobile oxygen and caused the high CO oxidation activity.

From the results of redox measurement at 200 °C and XPS, manganese might have been partially reduced from Mn⁴⁺ to Mn³⁺ in case of Meso-Mn. On the other hand, theoretical weight decrease from, for example, Cu_{0.5}²⁺Mn³⁺O₂ to Cu_{0.5}¹⁺Mn²⁺O_{1.25} or Cu_{0.5}²⁺Mn⁴⁺O_{2.5} to Cu_{0.5}¹⁺Mn³⁺O_{1.75} is about 10 wt%. Therefore, it is estimated that both manganese and copper [32] were reduced in case of copper-containing mesoporous manganese oxide prepared by the sol–gel method.

4. Conclusions

By the sol–gel method, copper-containing mesoporous manganese oxides having amorphous structure, about 6 nm mesopore and high copper dispersion, were prepared. Copper-containing mesoporous manganese oxides prepared by the sol–gel method showed higher CO oxidation activity than the commercial catalyst, Hopcalite. By incorporation of copper, electron transfer occurred between oxygen and manganese, leaving lattice oxygen species of different nature. One of these lattice oxygen species was very mobile, easy to be removed and reintroduced (high redox ability), and caused the higher CO oxidation activity. Increased CO adsorption was also a reason for the high CO oxidation activity.

Acknowledgment

Part of this work was supported by a grant in Aid from the High Technology Research Center Project of Kansai University.

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